

The University of Chicago

THE NON-ISOMERIZATION OF FREE RADICALS IN SOLUTION

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
MARCH, 1943

By
RALPH LAWRENCE DANNLEY

CHICAGO, ILLINOIS

1943

The University of Chicago

THE NON-ISOMERIZATION OF FREE RADICALS IN SOLUTION

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
MARCH, 1943

By
RALPH LAWRENCE DANNLEY

CHICAGO, ILLINOIS

1943



ACKNOWLEDGMENT

The author is greatly indebted to Dr. M. S. Kharasch for his constant interest and invaluable advice during the course of this investigation.



Digitized by the Internet Archive
in 2026

THE NON-ISOMERIZATION OF FREE RADICALS IN SOLUTION

Introduction

A free radical is, by definition, an electrically neutral molecule with one or more unpaired electrons. Most of the polyatomic radicals hitherto observed show a strong tendency to react either with one another or with other molecules to form more stable compounds. From the rate of this stabilizing reaction, the so-called "half-life period" of the free radical is calculated. By comparison of these half-life periods, free radicals may be roughly divided into two classes. Triphenyl methyl¹ may be regarded as a typical member of the first class; methyl² as a typical member of the second.

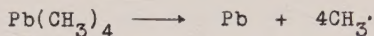
The members of the triphenyl methyl class are characterized by half-life periods ranging from a few hours to years. The presence of such radicals in solution has been proved by molecular weight determinations. The paramagnetic susceptibilities of the substances in question show that the free radicals exist in both the liquid and the solid states. Free radicals of this type have had but slight application in synthetic chemistry. No evidence as to their existence in the gaseous state has been presented.

Free radicals of the methyl type, on the other hand, were first demonstrated in the gaseous state. Paneth and his co-workers² showed that when certain metal alkyls are heated, the metal is deposited; at the same time there are formed certain substances which attack metal films if and only if they come into contact with such films very shortly after the moment of decomposition of the metal alkyl. For example, lead tetramethyl, when heated, deposits lead. At the same time, there is produced a substance which attacks nearby mercury films to form mercury dimethyl. By carrying out the decomposition of the metal alkyl at reduced pressure in a gas stream of measured velocity, and by regulating the distance between the point of decomposition and

¹Gomberg, J.A.C.S., 22, 757 (1900).

²Paneth and Hofeditz, Ber., 62, 1335 (1929).

the metal film to be attacked, Paneth was able to calculate the half-life period of the active component formed. This period, under the experimental conditions used, turned out to be of the order of 0.006 seconds. Paneth explained his results by assuming that lead tetramethyl decomposes as follows:



The methyl radicals then attack the mercury



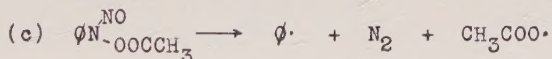
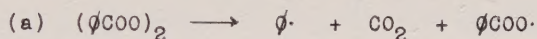
Paneth found that he could obtain results of the sort described only if he worked at very low pressures (about 2 mm.). He therefore assumed that the free alkyls reacted not only with metal films but also with one another or with the diluent gas. At high concentrations, destructive collisions between the radicals and other particles occurred so frequently that the radicals had vanished from the gas stream before their existence could be demonstrated. If these ideas are correct, it follows that free radicals of the type investigated by Paneth cannot be isolated in pure form. Only indirect evidence of their existence can be adduced. At the low pressures and concentrations used by Paneth, free radicals of the type which he investigated are present in such small amounts as to be useless for macroscopic syntheses.

Following Paneth's ideas, a radical which, in the gas phase, has a short life should, in the liquid phase, have an even shorter existence, because of the much greater probability of collision under the latter condition. It has been estimated³ that the half-lives of such free radicals in solution should not exceed 10^{-10} seconds.

The hypothesis of the existence of short-lived free radicals in solution is supported by the following evidence. (1) Many organic reagents of widely divergent types, if decomposed in a given solvent, react with that solvent to give identical products. (2) These same compounds, when dissolved in various solvents, decompose at a rate which is independent of the solvent used. Hey and Waters³ have published a summary of data obtained prior to

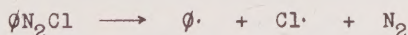
³Hey and Waters, Chem. Rev., 21, 169 (1937).

1938. They have called attention to the similarity of the products formed when (a) diacyl peroxides, (b) azotriarylmethanes (c) nitrosoarylamides and (d) diazohydroxides are decomposed in solution. A striking illustration is the behavior of aromatic compounds of the types mentioned, when these substances are decomposed in aromatic solvents. Under these circumstances, a hydrogen atom in the solvent is replaced by an aromatic radical (see Table 1). It is noteworthy that, in all the instances cited, the chief product is the meta or ortho derivative, irrespective of the directive influence of this group under the ordinary rules for substitution. Hey and Waters explained the results cited by assuming the intermediate formation of free phenyl radicals.



These phenyl radicals then replace a nuclear hydrogen in the aromatic solvent. It should be recollected that the ordinary rules for orientation in the benzene ring were originally established for reactions with anionoid or cationoid reagents. It is therefore interesting but not contradictory that the groups (nitro, aldehydo, etc.) which are meta-directing in reactions with cationoid reagents become ortho-para-directing when a different type of reagent (here a free radical) is used.

Pray⁴ investigated the thermal decomposition of phenyl diazonium chloride which he assumed to proceed as follows:



He carried out this reaction in various alcohols and acids, the molecules of which are attacked by the free radicals formed. Pray argues that, since the half-life period of these radicals in solution is very short, the rate-determining step should be the decomposition of the diazonium chloride. Hence the reaction rate should be first order with respect to the diazonium compound, and should be but little affected by the nature of the solvent. He

⁴Pray, J. Phys. Chem., 30, 1477 (1926).

TABLE 1

REACTIONS OF FREE RADICALS WITH AROMATIC SOLVENTS

Reagent	Type	Solv.	Product
Benzoyl peroxide	a	ϕCl	4-chlorobiphenyl ⁵
Phenylazotriphenylmethane	b	"	4-chlorobiphenyl ⁵
Nitroso acetanilide	c	"	4-chlorobiphenyl ⁶
Benzoyl peroxide	a	ϕNO_2	2- and 4-nitrobiphenyl ¹
Nitrosoacetanilide	c	"	2- and 4-nitrobiphenyl ⁶
Phenyldiazo hydroxide	d	"	4-nitrobiphenyl ⁷
Benzoyl peroxide	a	ϕCH_3	2- and 4-methylbiphenyl ⁸
Phenylazotriphenylmethane	b	"	2- and 4-methylbiphenyl ⁹
Nitrosoacetanilide	c	"	4-methylbiphenyl ⁶
Phenyldiazo hydroxide	d	"	2- and 4-methylbiphenyl ⁷
Benzoyl peroxide	a	$\text{C}_5\text{H}_5\text{N}$	2- and 4-phenylpyridine ¹⁰
Phenylazotriphenylmethane	b	"	2- and 4-phenylpyridine ⁹
Phenyldiazo hydroxide	d	"	2- and 4-phenylpyridine ¹¹

⁵Hey, J.C.S., 1966 (1934).

⁶Grieve and Hey, ibid., 1797 (1934).

⁷Gomberg and Bachmann, J.A.C.S., 46, 2339 (1924); Gomberg and Pernert, ibid., 48, 1372 (1926).

⁸Gelissen and Hermans, Ber., 58, 285 (1925).

⁹Wieland et al., Ann., 514, 145 (1934).

¹⁰Overhoff and Tillman, Rec. Trav. Chim., 48, 993 (1929).

¹¹Mohlau and Berger, Ber., 26, 1994 (1893).

found that, when his various solutions were heated, the rate of nitrogen evolution was proportional to the concentration of the diazonium chloride and nearly independent of the solvent used. This fact is the more noteworthy since the reaction with methyl alcohol is widely different from that with the other solvents used; yet the reaction in methyl alcohol has the same rate constant as the other reactions.



The identity of the rates supports Pray's explanation, since the further behavior of the very reactive free phenyl radical should not affect the rate of its formation.

Other studies have shown that, in excess solvent, the thermal decompositions of nitrosoacetanilide¹² and diacetyl peroxide¹³ are also first order with respect to these reagents.

When reagents which produce free radicals are decomposed in various aliphatic solvents, the products formed show the expected similarities. Usually, an aromatic free radical acting upon an aliphatic acid, alcohol, or hydrocarbon removes a hydrogen atom from the molecule of the solvent. Thus benzoyl peroxide reacts with ethyl alcohol, isobutyl alcohol, acetic acid, cyclohexane, and 2-pentene¹⁴ to yield benzene. When the same reagents are decomposed in nonaromatic organic halides such as carbon tetrachloride,¹⁵ tetrachlorethylene,¹⁶ or methyl iodide¹⁷ the free radical removes a halogen atom from the solvent to form the corresponding halide.

¹²Grieve and Hey, J.C.S., 1800 (1934).

¹³Walker and Wild, ibid., 1132 (1937).

¹⁴Gelissen and Hermans, Ber., 58, 765, 770, 2396 (1925); 59, 662 (1926).

¹⁵Boeseken and Gelissen, Rec. Trav. Chim., 43, 869 (1934).

¹⁶Reynhart, ibid., 46, 72 (1927).

¹⁷Waters, J.C.S., 113 (1937).

Free Radicals in Chain Reactions

When a free radical "B" attacks a neutral molecule, another free radical "C" is always formed. If "C" then attacks another neutral molecule and initiates a reaction which (either in the first or some subsequent step) produces another radical "B," then the single initial radical "B" may cause a large number of neutral molecules to react. Such a "chain" reaction may be epitomized by the following cycle:



The chain reaction continues until some side reaction interrupts the cycle. In the reaction cited, dimerization of either "B" or "C" would be such a chain-breaking mechanism. In particular instances it may be necessary to start such a chain by an initial step which is not thereafter repeated.



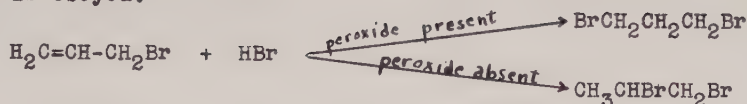
Here the free radical "A" (or the substance from which it was formed) would be called a chain initiator. In the absence of such an initiator, the components of the reaction mixture may react by a polar mechanism to give entirely different products.

Chain reactions in the vapor phase have been observed by many investigators. Kharasch and his co-workers have assigned chain mechanisms to many organic reactions in solution; some of the type reactions thus explained have been extensively investigated in this laboratory. Kharasch and Mayo¹⁸ found, for example, that, in the presence of peroxides, the addition of hydrogen bromide to olefines proceeds by a chain mechanism involving bromine atoms and free radicals.¹⁹ Here the direction of addition is not in accordance with Markownikoff's rule. In the absence of peroxides, the mechanism of the reaction is polar, and Markownikoff's

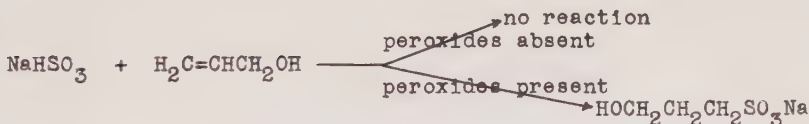
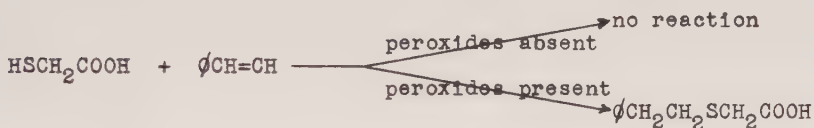
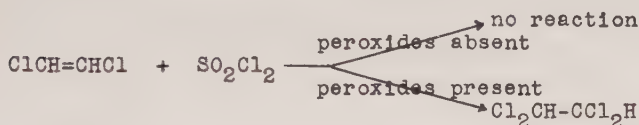
¹⁸Kharasch and Mayo, J.A.C.S., 55, 2468 (1933).

¹⁹Kharasch, Engelman, and Mayo, J. Org. Chem., 2, 288 (1937).

rule is obeyed.



The peroxide decomposes slightly even at room temperature into free radicals which start the chain involving free bromine atoms; the peroxide is thus a chain initiator. Similar chain reactions requiring an initiator have been observed in the chlorination of aliphatic substances with sulfuryl chloride,²⁰ in the addition of mercaptans²¹ and bisulfites²² to unsaturated compounds, and in certain molecular rearrangements.²³



Reaction rapid in the presence of peroxides but slow in their absence.

Peroxides are not the only substances which, acting as chain initiators, exercise profound effects similar to those noted above. Thus, in the presence of metallic iron, hydrogen bromide

²⁰Kharasch and Brown, J.A.C.S., 61, 3432 (1939).

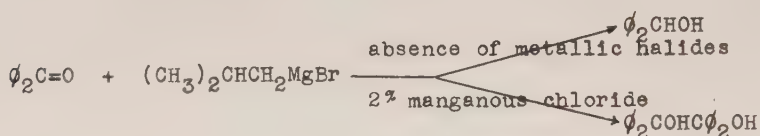
²¹Kharasch, Read and Mayo, Chem. and Ind., 57, 752 (1938).

²²Kharasch, May and Mayo, J. Org. Chem., 3, 175 (1938).

²³Kharasch, Margolis and Mayo, ibid., 1, 393 (1936).

adds to some unsaturated alkyl halides to give products which are not those predicted in accordance with Markownikoff's rule.²⁴ Sodium nitrite or ammonium nitrite may be substituted for a peroxide as a chain initiator in the addition of bisulfites to liquid alkenes.²⁵

Small quantities of metallic halides completely alter the course of some Grignard reactions²⁶ by causing the reaction to proceed by a free radical instead of a polar mechanism. An example is the following:



Such chain reactions are of great importance, not only because they account for the formation of unusual by-products in the presence of certain impurities, but also because, in synthetic work, they offer the possibility of obtaining new products from easily accessible compounds.

Isomerization of Free Radicals

It has been thought that, where isomeric free radicals are possible, isomerization to the most stable form might occur before the radical reacted with a neutral molecule. Such rearrangements would be most probable in the vapor phase, since, in that phase, the half-life period of a radical is longer than in the liquid phase. Glazebrook and Pearson²⁷ report that free isopropyl radicals (prepared by the photolysis of diisopropyl ketone vapors) isomerize to normal propyl radicals before they react with mercury. They also ascribe to free radical isomerization the partial conversion of n-propyl bromide vapors to isopropyl

²⁴Kharrasch, Haefele and Mayo, J.A.C.S., 62, 2047 (1940).

²⁵Schenck, Ph.D. dissertation, University of Chicago (1940).

²⁶Kharrasch, Kleiger, Martin and Mayo, J.A.C.S., 63, 3405 (1941).

²⁷Glazebrook and Pearson, J.C.S., 1777 (1936).

bromide at 262° ,²⁸ and the liquid phase conversion of isobutyl bromide to tertiary butyl bromide under the influence of ultra-violet light.²⁹

The term "isomerization" applied to free radicals usually implies "tautomerization," for in most cases nothing but the shift of a hydrogen atom and the accompanying electronic rearrangement is involved. Hence, in view of the great reactivity of free radicals in solution, it is improbable that such a tautomeric shift can occur before an effective collision of the free radicals with a neutral molecule has taken place. To verify this prediction, Kharasch, Kane and Brown³⁰ decomposed normal butyryl peroxide and isobutyryl peroxide in carbon tetrachloride; they discovered no evidence of any rearrangement of the free radicals. Decomposition of normal butyryl peroxide yielded only normal propyl chloride; no trace of isopropyl chloride was found. Likewise, the decomposition of isobutyryl peroxide gave only isopropyl chloride, with no trace of normal propyl chloride. Evidently, in the reactions studied, the aliphatic free radicals in solution do not isomerize.

No aromatic free radical has as yet been observed to isomerize, but since no great amount of work has been done in this field, the interconversion of alpha and beta naphthyl free radicals might still be regarded as a possibility. Alpha and beta naphthylazotriphenylmethane have been decomposed in carbon tetrachloride³¹ to yield respectively alpha and beta chloronaphthalene. The yields reported are, however, too small to be used as evidence against rearrangement. Hey and his co-workers have done considerable work with the decompositions of nitroso aceto beta naphthylamide and some of its substituted analogues. Yields of products up to 52 per cent have been recorded; no mention is made of the isolation of rearranged products. The results of their work are given in Table 2.

²⁸Eltekoff, Ber., 6, 1258 (1873); 8, 1244 (1875); Michael and Leupold, Ann., 379, 263 (1911).

²⁹Lucas and Salmon-Legagneur, Compt. Rend., 186, 39 (1928).

³⁰Kharasch, Kane and Brown, J.A.C.S., 63, 526 (1941).

³¹Wieland et al., Ann., 514, 145 (1934).

TABLE 2
DECOMPOSITIONS OF SUBSTITUTED NITROSO ACETO BETA
NAPHTHYLAMIDE IN VARIOUS SOLVENTS

Ref.	Compound	Solvent	Products
(a)		$\emptyset$ H	25%
(a)		$\emptyset$ NO ₂	40%
(b)		$\emptyset$ H	40%
(b)		$\emptyset$ H	47%
(b)		$\emptyset$ H	52%
(b)		$\emptyset$ H	44%

32 (a) Elks, Hayworth and Hey, J.C.S., 1284 (1940).

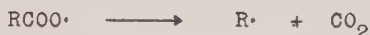
33 (b) Hey and Lawton, ibid., 374 (1940).

Discussion

Aliphatic acyl peroxides invariably decompose to yield a minimum of one mol of carbon dioxide per mol of peroxide used. This fact indicates that the first step in the decomposition is



Under the influence of heat, or by reaction with another molecule, the acyloxy radical may also decompose to yield additional carbon dioxide.



Yields up to 1.5 mols³⁴ of carbon dioxide per mol of peroxide have been obtained. Aromatic acyl peroxides in solution usually yield one mol of carbon dioxide per mol of peroxide. However, in one observed instance, namely, the decomposition of benzoyl peroxide in diisopropyl ether,³⁵ no carbon dioxide is evolved, and all of the peroxide is converted to benzoic acid. This finding suggests a second possible mechanism for the decomposition of aromatic acyl peroxides. The first step may be a cleavage to two acyloxy radicals which may react directly with the solvent.



Under most conditions, however, the second steps should be the decomposition of part of the acyloxy radicals into carbon dioxide and free aryl radicals.



This second step is identical with the second step in the decomposition of aliphatic acyl peroxides. So far there is no evidence for the cleavage of aliphatic acyl peroxides into two acyloxy radicals.

In solution, the final products of the decomposition of acyl peroxides are the substances formed by the attack of the free radicals either upon the solvent or upon one another. Boeseken and Gelissen¹⁵ investigated the reactions of benzoyl per-

³⁴Kharasch and Gladstone, *J.A.C.S.*, **65**, 16 (1943).

³⁵Kharasch and Fineman, unpublished work.

oxides with carbon tetrachloride and chloroform. They report the nature but not the quantities of the products found. Among the products of the reaction with carbon tetrachloride, they identified phosgene, carbon dioxide, hexachlorethane and benzene. A little phthalic acid was obtained after hydrolysis of the crude reaction product with water. An additional substance which may have been either omega trichlor para toluic acid or trichloromethyl benzoate, was also isolated. Hydrolysis of this compound yielded terephthalic acid, but the authors suggest that the trichloromethyl group may have migrated to the nucleus during the hydrolysis.

In the present investigation, both alphanaphthoyl peroxide and beta naphthoyl peroxide were thermally-decomposed in carbon tetrachloride. The products isolated are listed in Tables 3 and 4. These findings show that, at the temperature of boiling carbon tetrachloride, there is no isomerization of the free radicals in solution. Both alpha and beta naphthoyl peroxides yield approximately one mol of carbon dioxide per mol of peroxide. The naphthyl free radical attacks the solvent to form chloronaphthalene.



The presence of alpha naphthoyl chloride among the final products obtained from alpha naphthoyl peroxide may be explained as follows:



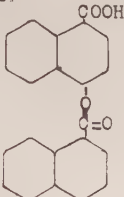
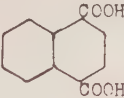
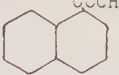
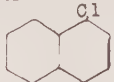
This decomposition of the trichloromethyl ester to the acid chloride is analagous to the thermal decomposition of diphosgene to phosgene.



The free trichloromethyl radical also takes part in a side reaction. It attacks the aromatic nucleus and forms a trichloromethyl-substituted aromatic molecule which, upon hydrolysis, yields a naphthalic acid. This side reaction has been observed

TABLE 3

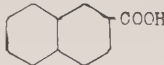
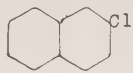
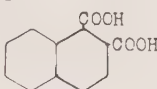
ANALYSIS OF ALPHA NAPHTHOYL PEROXIDE DECOMPOSITION
ON THE BASIS OF ONE MOL OF PEROXIDE USED

Moles of peroxide used	1.000
Moles of carbon dioxide evolved	.911
Moles of 	.111
Moles of 	.015
Moles of 	.762
Moles of 	.756
Moles of hexachlorethane	.088
Moles of chloride ion	.950
Moles of peroxide accounted for	.877

When the entire reaction mixture was vacuum distilled, 0.381 mols of alpha naphthoyl chloride per mol of peroxide used was obtained in the distillate.

TABLE 4

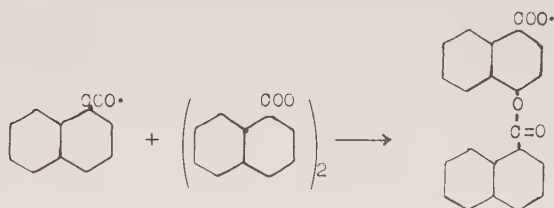
ANALYSIS OF BETA NAPHTHOYL PEROXIDE DECOMPOSITION
ON THE BASIS OF ONE MOL OF PEROXIDE USED

Moles of peroxide used	1.000
Moles of carbon dioxide evolved	.914
Moles of 	1.032
Moles of 	.811
Moles of 	.075
Moles of hexachlorethane	.018
Moles of chloride ion	1.428
Moles of peroxide accounted for	.959

in the decompositions of both alpha and beta naphthoyl peroxides. In each instance, the amount of chloride ion found in the reaction products corresponds roughly to the amount calculated to be produced by hydrolysis of the acid chlorides and the trichloromethyl naphthoic acid. Boeseken and Gelissen obtained a trichloromethyl naphthoic acid as one of the main products in their benzoyl peroxide decompositions, probably because they worked with very concentrated solutions.

The small quantity of hexachlorethane isolated in the experiments here described is no doubt formed by the dimerization of two free trichloromethyl radicals.

The formation of one more product, para alpha naphthoyloxy alpha naphthoic acid, is yet to be explained. This compound is probably formed when an acyloxy radical attacks an aromatic nucleus. The reaction may proceed as follows:



The last-named compound is of interest, because, in no previously investigated decomposition of an acyl peroxide in solution, has the free acyloxy radical been observed to substitute in an aromatic nucleus. If the solvent molecule contains hydrogen, such radicals usually remove hydrogen atoms and go over to the corresponding acids. The only known exceptions to this rule are the reactions of acetyl and propionyl peroxides when decomposed in isopropyl ether.³⁶ Here the free radical removes an isopropyl group from the solvent and forms the isopropyl ester.



The point of attack of free radicals upon substituted naphthalene nuclei has not previously been determined. The ortho-

³⁶Kharasch and Fineman, unpublished work.

para substitution invariably observed in attacks upon benzene derivatives has been described. The only substituted polynuclear compounds which have hitherto been the subjects of similar investigations are the biphenyl derivatives.³⁷ Here again only ortho-para substitution has been observed.

Certain of the products isolated in the present investigation can hardly have been formed by any method other than the attack of a free radical on the naphthalene nucleus. The following shows the results obtained.

Free radical	Nucleus attacked	Product isolated
$\text{CCl}_3^\bullet$		
$\text{CCl}_3^\bullet$		

The trichloromethyl derivatives first formed were hydrolyzed to the corresponding acids in the course of the process of isolation. It should be noted that, if the naphthalene compound contains a hydrogen atom para to the substituent, this para atom is the one replaced by the entering free radical. Where the para position is blocked, the free radical replaces the alpha hydrogen atom ortho to the substituent.

³⁷Grieve and Hey, J.C.S., 108 (1938).

The Method of Decomposing the Peroxides

The apparatus in which the peroxides were decomposed is shown in Figure 1. The three-liter reaction vessel "A" contained about 1500 cc. of boiling carbon tetrachloride. A suspension of 15 to 50 grams of peroxide in 200 to 400 cc. of carbon tetrachloride was placed in the dropping funnel "B" and constantly agitated by a stirrer, to prevent settling. Over a period of hours, this suspension was run, in successive small portions, into the reaction flask. The object of this slow addition was to keep the free radical concentration in the boiling solution low. By this means, dimerization of the free radicals was minimized, and reaction with the solvent molecules promoted.

Trap "D" was cooled to -80° with dry ice in order to condense any carbon tetrachloride and volatile reaction products which might have passed through the water condenser "C." The carbon dioxide evolved in the reaction was absorbed by the soda-lime in the U-tubes, "F," "G," "H." The increase in weight of these U-tubes was taken as the weight of the carbon dioxide evolved. In no run, was any gas collected in the water-filled flask "J" at the end of the train. Hence, all volatile products of the reaction were collected in "D," "E," or "F," "G," "H." At the conclusion of each run, trap "E" was cooled in dry ice, and "D" was warmed to room temperature. This step was taken in order to separate extremely volatile products from those which are liquid at room temperature. Actually, carbon tetrachloride was the only substance ever found in either trap. Finally, carbon-dioxide-free air was drawn through the entire system in order to sweep all the evolved carbon dioxide into the U-tubes.

Preparation and Decomposition of Alpha Naphthoyl Peroxide

Preparation of alpha naphthoyl chloride.--Alpha naphthoyl chloride was prepared by refluxing 75 grams of alpha naphthoic acid with 100 cc. of thionyl chloride for two hours. After the excess thionyl chloride had been distilled off at atmospheric pressure, the product was distilled in vacuo. Seventy-five to eighty grams (93 to 96 per cent) of the acid chloride were obtained (b.p. $172-173^{\circ}/15$ mm.).

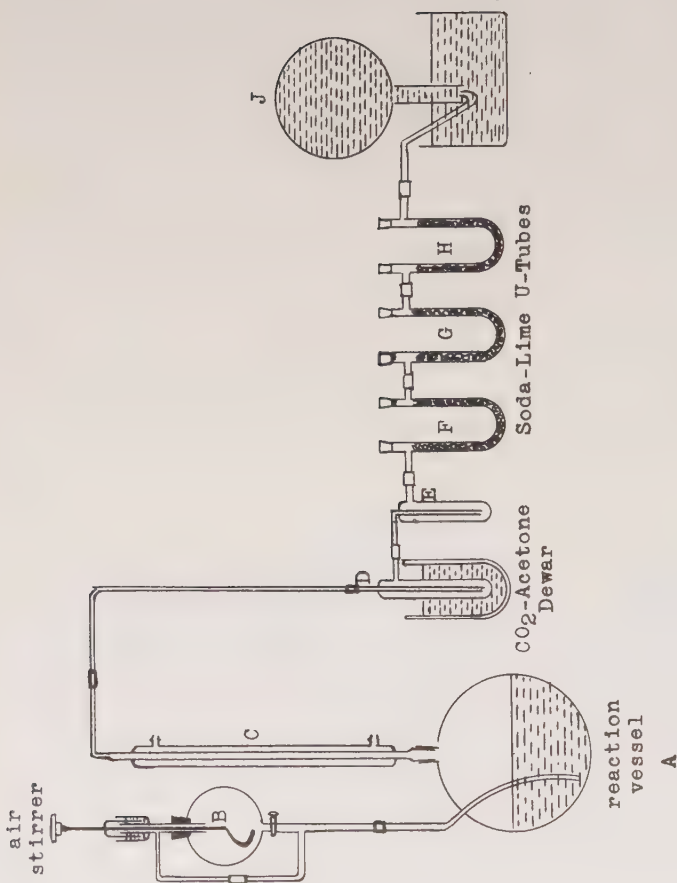


Figure 1

Preparation of alpha naphthoyl peroxide.--Thirty-five grams of alpha naphthoyl chloride were dissolved in 50 cc. of anhydrous acetone; the solution was then added slowly to a vigorously stirred suspension of 7.4 grams of sodium peroxide in 100 cc. of anhydrous acetone. The temperature was not allowed to rise above zero degrees. After the addition of the acid chloride was complete, one cubic centimeter of water was added. Stirring at zero degrees was continued overnight. The alpha naphthoyl peroxide separated as a white precipitate. The entire mixture was poured into 200 cc. of water to decompose the excess sodium peroxide. The alpha naphthoyl peroxide was collected on a filter. It was then dissolved in dioxane at room temperature, and fractionally precipitated by the addition of successive small amounts of water. The yield of purified product was 15 to 20 grams (46 to 62 per cent). The purity (determined iodometrically³⁸) ranged from 89 to 95 per cent. An especially pure sample was prepared by diluting an acetone solution with water. Its decomposition point was 98.2°. The figure given in the literature is 92°.

Decomposition of alpha naphthoyl peroxide in carbon tetrachloride.--A suspension of 16.81 grams of alpha naphthoyl peroxide (91 per cent pure) in 400 grams of carbon tetrachloride was added slowly, over a period of six hours, to 1700 grams of boiling carbon tetrachloride. At intervals during the addition, aliquot portions of the reaction mixture were removed and titrated. At no time was there more than one-half gram of undecomposed peroxide present in the entire boiling solution. After all the peroxide had been added, the refluxing was continued for twelve hours. At the end of this time, 1.80 grams of carbon dioxide had been collected in the U-tubes. When the reaction mixture was chilled, 1.61 grams of material (I) (later identified as para alpha naphthoxy alpha naphthoic acid) separated out. Most of the carbon tetrachloride was then distilled from the reaction mixture at atmospheric pressure. When the residue (50 cc.) was cooled, an additional 0.09 grams of (I) was obtained. The residue was then refluxed for twelve hours with water to hydrolyze any acid chloride which might be present. Steam distillation of the hydrolyzed material yielded a mixture (II) of carbon tetrachloride, hexachlorethane, and alpha chloronaphthalene. When the supernatant

³⁸Kokatnur and Jelling, J.A.C.S., 64, 1432 (1941).

aqueous layer of the residue from steam distillation was cooled, 0.18 grams of material (III) separated out. This proved to be a mixture of alpha naphthoic acid and 1,4 naphthalic acid. The water insoluble residue from the steam distillation was refluxed with 100 cc. of water and 4 grams of sodium hydroxide for eighteen hours. The aqueous alkaline solution was extracted with ether. The ether extract, when evaporated, yielded 1.96 grams of tar (IV). When the aqueous alkaline solution was acidified with sulfuric acid, a precipitate was formed. This was separated by filtration. The acidified solution was extracted with ether and the ether extract added to the precipitate. By this means, there was obtained 5.36 grams of material which was identified as alpha naphthoic acid (V). Titration (Volhard) of the acidified aqueous solution showed the presence of 0.0425 mols of halide.

Identification of the Products Formed
in the Decomposition of the
Alpha Naphthoyl Peroxide

Fraction I.--After this fraction had been twice recrystallized from toluene, it consisted of white crystals melting at 229.9-230.4° (corrected). The melting point was unchanged by recrystallization from dioxane-water. The compound was insoluble in hot water and ligroin but soluble in aqueous alkali. Fusion with sodium showed that no halogen was present. The compound was hydrolyzed with dilute aqueous sodium hydroxide, and the alkaline solution was then acidified with mineral acid. A precipitate (VI) (presumably organic acids) separated out. This material was collected on a filter and dried. One portion was refluxed with thionyl chloride to convert the acids to the acid chlorides. Vacuum distillation of the product yielded a low melting white solid which was treated with aqueous alkali. When the alkaline solution was acidified, a precipitate formed. This precipitate, after it had been recrystallized from ligroin, melted at 158-158.5°. Its neutralization equivalent was 174. The material did not depress the melting point of a known sample of alpha naphthoic acid (M.P. 159-160°, neutralization equivalent 172).

Another portion of precipitate (VI) was mixed with lime and subjected to dry distillation. The product was a white solid which, when recrystallized from hot water, melted at 92-92.5°, and did not depress the melting point of a known sample of alpha

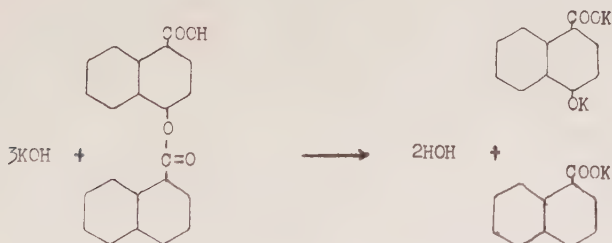
naphthol (M.P. 93.5-94°). It was suspected that the parent compound from which this alpha naphthol had been formed was para hydroxy alpha naphthoic acid. This acid can readily be nitrated. A 0.15 gram sample of the mixture (VI) was, therefore, dissolved in 1 cc. of glacial acetic acid, cooled to 0°, and treated with 0.15 cc. of nitric acid. After the mixture had stood ten minutes, a precipitate formed. This was removed by filtration, dissolved in sodium carbonate, and reprecipitated with dilute hydrochloric acid. It was finally recrystallized from acetic acid. The bright yellow crystals melted with decomposition at 255°. The decomposition point of 3-nitro-4-hydroxy alpha naphthoic acid is 258°. ³⁹ When another portion of (VI) was recrystallized from hot water, crystals melting at 182-184° (sealed tube) were obtained. The melting point of para hydroxy alpha naphthoic acid is 183-184°.

The identification of the above-mentioned hydrolysis products of Fraction (I) made it probable that this material was para alpha naphthoxyloxy alpha naphthoic acid (A). The analysis of Fraction (I) supported this assumption.

Anal. Calc'd. for $C_{22}H_{14}O_4$: C, 77.40; H, 4.10; Mol.

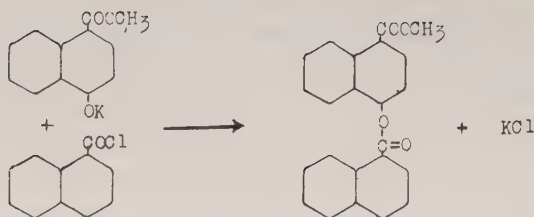
Wt., 342. Found: C, 76.70 and 77.36; H, 4.49 and 4.66; Mol. Wt., 310.

(A) should be hydrolyzed as follows:



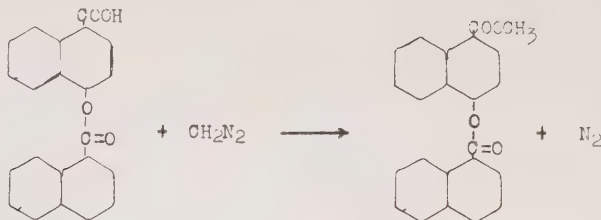
The synthesis of this compound from para hydroxy alpha naphthoic acid and alpha naphthoyl chloride was therefore attempted. This attempt failed, but the following synthesis of the corresponding methyl ester was successful.

³⁹ Heller, Ber., 45, 676 (1912).



Five grams of the methyl ester of para hydroxy alpha naphthoic acid⁴⁰ were dissolved in 25 cc. of 8 per cent aqueous potassium hydroxide. While the solution (chilled to 0°) was violently stirred, 5 cc. of alpha naphthoyl chloride were added. After the addition was complete, the mixture was stirred for two hours. The solid product was collected on a filter and recrystallized, first from toluene, and finally from acetone. The white crystals (3.3 grams, 37 per cent of the theoretical yield) thus obtained, melted at 132-133.2°.

A portion of Fraction (I), dissolved in ether, was treated with diazomethane.



Recrystallization of the product from toluene gave white crystals which melted at 132.8-134°.

Anal. Cal'd for $\text{C}_{23}\text{H}_{16}\text{O}_4$: C, 77.50; H, 4.49. Found:
C, 77.44; H, 4.77.

This material did not depress the melting point of the pure methyl ester of (A) synthesized above. The structure of the material composing Fraction (I) is thus determined.

Fraction II.--Fraction (II) was shown to be a mixture of carbon tetrachloride, hexachlorethane, and alpha chloronaphthalene. Vacuum distillation readily separated the carbon tetrachloride

⁴⁰Friedlander, 14, 729 (1921).

from the other components, but was not suitable as a quantitative method for separating the chloronaphthalene from the hexachlorethane. The hexachlorethane and alpha chloronaphthalene were, therefore, distilled as one fraction (VII) (6.43 grams); the halogen content of this fraction was determined (Parr bomb). Hexachlorethane and alpha chloronaphthalene contain respectively 90.0 per cent and 21.85 per cent chlorine. Fraction (VII) contained 31.73 per cent halogen, corresponding to 85.5 per cent alpha chloronaphthalene (5.50 grams) and 14.5 per cent hexachlorethane (.93 grams). The qualitative separation of these constituents for purpose of identification was accomplished by means of a vacuum distillation in which a middle fraction, corresponding to 10 per cent of the total material, was discarded. The first fraction was a white solid which melted at 183-184°; its melting point was not depressed by addition of hexachlorethane (M.P. 184°). The last fraction was a liquid with an index of refraction 1.6323^{20°}. The index of refraction of alpha chloronaphthalene is 1.6332^{20°}.

Fraction III.--Fraction (III) was shown to consist of a mixture of alpha naphthoic acid and 1,4-naphthalic acid. The material, which had a neutralization equivalent of 143.1 (corresponding to 78.9 per cent of the 1,4-naphthalic acid and 21.1 per cent alpha naphthoic acid), was extracted with hot toluene to remove the alpha naphthoic acid. The residue, which decomposed at 235-240°, had a neutralization equivalent of 112.8. Treatment of this residue with diazomethane gave a compound which, when recrystallized from ligroin, melted at 59.5-61°. These constants identify the material as 1,4-naphthalic acid which has a neutralization equivalent of 108, a decomposition point of 240°, and a dimethyl ester which melts at 64°. When the toluene extract was cooled, a white crystalline solid (M.P. 158.5-159.5°) separated out. A known sample of alpha naphthoic acid (M.P. 160°) did not depress the melting point of this material.

Fraction IV.--Since this fraction was not attacked by boiling aqueous alkali and could not be steam distilled, it was thought to consist of high molecular weight compounds. Since an attempt to sublime this material at low pressure proved unsuccessful, no further work was done with it.

Fraction V.--This fraction was proved to consist of alpha naphthoic acid. A potentiometric titration of the material showed

it to have a neutralization equivalent of 170. The neutralization equivalent of alpha naphthoic acid is 172. The material was purified by treating it with thionyl chloride. The reaction product was distilled in vacuo, and the distillate hydrolyzed with aqueous alkali. The precipitate obtained by acidification of the alkaline solution was recrystallized from toluene. The recrystallized material melted at 157-159°; its melting point was not depressed by the addition of alpha naphthoic acid (M.P. 159-160°).

Alternative Analysis of Alpha Naphthoyl Peroxide Decomposition Products

In a run similar to the one just described, 38 grams of alpha naphthoyl peroxide were decomposed in 1800 grams of boiling carbon tetrachloride. Carbon tetrachloride and para alpha naphthoxy alpha naphthoic acid were removed from the reaction product in the manner already described. Vacuum distillation of the residue yielded two fractions. The first (12.5 grams; b.p., 119-122° at 12 mm.) was identified as a mixture of hexachlorethane and alpha chloronaphthalene. The second (6.1 grams; b.p., 160° at 12 mm.) was identified as alpha naphthoyl chloride. The acid chloride which was used in the preparation of alpha naphthoyl peroxide was shown to boil at 163° at 12 mm. The material under investigation, when hydrolyzed with alkali, yielded a crystalline material which melted at 158-159°. This melting point was not depressed when the material was mixed with alpha naphthoic acid (M.P. 160°).

Preparation and Decomposition of Beta Naphthoyl Peroxide

Preparation of beta naphthoyl chloride.--Seventy-five grams of beta naphthoic acid and 100 cc. of thionyl chloride were refluxed on a steam bath for four hours. The excess thionyl chloride was distilled off at atmospheric pressure; the residue was distilled in vacuo. A yield of 52 to 71 grams (62 to 85 per cent) of the acid chloride (b.p. 173-174°/20 mm.) was obtained. This material, after recrystallization from high boiling ligroin, melted at 51°.

Preparation of beta naphthoyl peroxide.--The preparation of beta naphthoyl peroxide is in all respects similar to that of alphanaphthoyl peroxide, and was carried out with the same quanti-

ties of materials (cf. p. 19). The purification of the crude product, however, was somewhat easier. Washing this material, first with dioxane and then with low boiling petroleum ether, was sufficient to give a product of purity higher than 88 per cent. A yield of 17 to 22 grams (54 to 70 per cent) of beta naphthoyl peroxide was thus obtained. A sample, the peroxide content of which was 96.5 per cent by titration, decomposed sharply at 138° .

Decomposition of beta naphthoyl peroxide in carbon tetrachloride.---A suspension of 29.98 grams of beta naphthoyl peroxide (96.5 per cent pure) in 350 grams of carbon tetrachloride was added slowly, over a period of ten hours, to 1500 grams of boiling carbon tetrachloride. After the addition was complete, refluxing was continued for an additional eight hours. At the end of this time, titration of an aliquot portion of the reaction mixture showed that less than one gram of peroxide remained undecomposed. The carbon tetrachloride was distilled off at atmospheric pressure, and the residue steam distilled. A yield of 11.67 grams of a solid mixture (I) (which proved to be beta chloronaphthalene and hexachlorethane) was obtained by filtration of the steam distillate. The aqueous distillate contained very little chloride ion. The tarry residue from the steam distillation was extracted with water in a Soxhlet apparatus for 16 hours. The aqueous extract, when concentrated and cooled, deposited 1.95 grams of a crystalline mixture (II), which proved to be beta naphthoic acid and 1,2-naphthalic acid. The water insoluble residue from the Soxhlet extraction was boiled with concentrated alkali. Extraction of the alkaline aqueous solution with ether, and evaporation of the ethereal extract, yielded 3.73 grams of a dark red oil (III). The aqueous alkaline solution; on acidification with sulfuric acid, gave 13.96 grams of beta naphthoic acid (IV). Extraction of the aqueous acid solution with ether, and evaporation of the ether, yielded an additional .79 grams of 1,2-naphthalic acid (V). A Volhard titration of the aqueous acid solution showed that 0.1481 mols of chloride ion were present. The increase in weight of the soda lime tubes showed that 3.46 grams of carbon dioxide were given off during the peroxide decomposition.

Identification of the Products of Decomposition of
Beta Naphthoyl Peroxide in Carbon Tetrachloride

Fraction I.---A Parr bomb analysis of Fraction (I) showed

this material to contain 24.2 per cent chlorine, corresponding to the chlorine content of a mixture of 96.6 per cent beta chloronaphthalene and 3.4 per cent hexachlorethane. These two substances were separated qualitatively by fractional distillation of the mixture. The beta chloronaphthalene thus obtained melted at 58° ; the hexachlorethane at $182-183^{\circ}$. The corresponding melting points given in the literature are $58-61^{\circ}$ and 184° .

Fraction II.--The neutralization equivalent of the material composing this fraction was 146. This figure corresponds to that of a mixture of 70 per cent beta naphthoic acid and 30 per cent of a naphthalic acid. When this mixture was recrystallized from high boiling ligroin, the crystalline product melted at $174-176^{\circ}$, and had a neutralization equivalent of 175. Beta naphthoic acid melts at 184° , and has a neutralization equivalent of 172. By evaporation of the mother liquor from the ligroin recrystallization, there was obtained a yield of crystals which sintered at 169° , and melted completely at 176° . The neutralization equivalent of this material was 122. These constants correspond to those of 1,2-naphthalic acid, which melts at 175° to give the anhydride, and has a neutralization equivalent of 108.

Fraction III.--When an attempt was made to sublime fraction (III) in vacuo, the material decomposed.

Fraction IV.--An aqueous solution of fraction (IV) was too deeply colored to permit its titration with indicators. Its neutralization equivalent was therefore determined potentiometrically. This equivalent was 172.3; that of beta naphthoic acid is 172. The purification of the crude material was difficult. A sample was treated with thionyl chloride and the product distilled in vacuo. Hydrolysis of the distillate yielded white crystals which melted at $173-176^{\circ}$. Recrystallization from toluene raised the melting point of this material to $176-178^{\circ}$; the purified substance had a neutralization equivalent of 170.5. Addition of beta naphthoic acid (melting point $179-180^{\circ}$) to this material did not depress its melting point.

Fraction V.--The crude fraction (V) was washed with a little ether to remove some oil adherent to the solid. The residue had a melting point of 177° and a neutralization equivalent of 112. The neutralization equivalent of 1,2-naphthalic acid is 108; the compound melts at 175° .

Conclusions

1. The evidence obtained indicates that the free alpha and beta naphthyl radicals in boiling carbon tetrachloride do not isomerize into one another.

2. One of the products found is probably formed when a free acyloxy radical, derived from a peroxide, attacks an aromatic ring. No similar reaction has previously been reported.

3. The point of attack of free acyloxy and trichloromethyl radicals upon the substituted naphthalene nucleus has been determined. This point, in all observed instances, is ortho or para to this substituent.

4. A mechanism for the reaction of aromatic acyl peroxides with carbon tetrachloride is suggested; evidence to support this suggestion is given.

